Consequence Study on Toxicity of

Carbon Dioxide Release in Seawater

By

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14306

Dissertation submitted in partial fulfillment of
the requirement for
Bachelor of Engineering (Hons)
(Chemical Engineering)

SEPTEMBER 2014

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the Chemical Engineering Programme
Universiti Teknologi PETRONAS

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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SITI AISHAH BT KHALED

TABLE OF CONTENT

LIST OF FIGURES

LIST OF TABLES

ABSTRACT

Consequence study of carbon dioxide release in seawater is becoming the one of the prevailing environmental concerns in this recent decade, mainly due to its potential harm to the ecosystem as well as the livelihood of the people whom depends upon it. Normally, carbon dioxide release is likely to take place in naturally occurring seabed fracture or man-made structure such as underwater carbon sequestering region or pipeline rupture. According to past simulation done by preceding experts, the majority of the results describes that the carbon dioxide plume tend not to escape to the surface of the seawater and is usually localized or confined in within certain boundary if the tidal mixing effect is minimal. Most of the modeling of carbon dioxide behavior done is based on the respective mathematical correlation or formulation designed to increase accuracy and reliability. However, for the sake of simplicity and compatibility with the scope of this project, the behavior of carbon dioxide toxicity release in seawater will be modeled using ANSYS Fluent Simulation Software using pertinent data acquired from other peer-reviewed research paper done by Fadzil (2012) and Dissanayake (2012). The location of the scenario chosen for this simulation is within the vicinity of South China Sea, as it is currently the target area for carbon capture storage system by the Malaysian authority. From the simulation of sub-seabed leakage, it is found that the simulation result is in great conformance with the physiochemical modeling of carbon dioxide release in seawater conducted by Dewar et al (2013). The maximum concentration of carbon dioxide and dispersed plume height rise acquired are 8.50E+09 ppm and 75.12 m respectively, yielding percentage errors of less than 10% for both of the parameters. However, pipeline leakage scenario is not taken into account to the due lack of experimental and simulation data for model verification and validation. The result obtained from this simulation is hoped to be utilized by any party involved in Carbon Sequestration and Storage System Project in Malaysia as value-added data.

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

This project is related to the consequence study on toxicity of carbon dioxide release in seawater focusing on modeling the behavior of carbon dioxide dispersion via pipeline leakage. There have been various formulation or models proposed by previous proponents of this subject in their endeavor accurately simulate the behaviour of carbon dioxide dispersion with seawater as its medium such as Finite Volume Coastal Ocean Model (FVCOM) (Blackford et al. 2013), MEGA_DEEP (Yap et al. 2010), OCEAN_CO_2(Dissanayake et al. 2012), and so on. However, these models were programmed to suit the given carbon dioxide leakage prone regions such as North Sea (Dewar et al, 2013), Shane Seep (Leifer et al, 2006), North West European Shelf (Blackford et al, 2013) and Kagoshima Bay (Dissanayake et al, 2012). However, it hardly covers the issue of pipeline leakage as the main focus of those studies revolves on underwater leakage from natural or artificial carbon dioxide storage system. For that reason, the central thesis of this research is to develop the most reliable model for carbon dispersion simulation that is compatible to local condition, especially for pipeline leakage. This study will mainly centers upon the assumptions as well as the correlation involves in building the model so that it can account for most scenarios possible in ensuring that the reliable prediction can be made based on the model.

1.2 PROBLEM STATEMENT

Underwater carbon dioxide leakage, in this era, has been gaining momentums of attention over the years due to its potential hazard it will bring upon the equilibrium of the environment. One of the causes which have been known to lead to such as incident is the underwater seabed leakage and offshore pipeline rupture. This will only add to ever worsening acidification of the ocean which is already contributed by absorption of the terrestrial discharge of carbon dioxide to the atmosphere. As a matter of fact, the world is beginning to witness the largest recorded value of acidity of the sea in the global history that is well over 380 ppmv (Petit et al. 1999) and this alone was contributed by the terrestrial discharge of carbon dioxide. As for underwater carbon dioxide discharge, recent estimate of release rate made by Harata et al. (2010) is around 48,500 tonnes per year. In addition, a study conducted by Kano et al. (2009) show that the leakage rate can achieve up to 94,600 tonnes per year in extreme cases and 3800 tonnes per year in moderate cases. This is indeed worrying considering the fact that this will create a surplus of carbon dioxide content in seawater and in turn, expose the marine life various ecological and biological threats such coral bleaching and narcosis. Long term exposure will result in the increase in mortality rate among aquatic organisms due to lower metabolic rate as well as having damaging effects towards the activity, growth and reproduction.

1.3 OBJECTIVE

The objectives of this project are:

1. To develop Computational fluid dynamics that can aptly describes behavior of carbon dioxide release in seawater
2. To validate the developed model in order to make accurate predictions based on available published data.

1.4 SCOPE OF STUDY

The simulation will make use of ANSYS FLUENT for modeling and simulation. The following parameters will be taken into consideration for modeling process:

1. Development of Fluid Domain
2. Computational Fluid Dynamics
3. Simulation Setting and Conditions
4. Verification and validation of results

CHAPTER 2

LITERATURE REVIEW

2. 1 THREATS OF HIGH CARBON DIOXIDE CONCENTRATION TO AQUATIC LIFE

High concentration of carbon dioxide poses a major disadvantage on the quality of nature. Apart from being a greenhouse gas emission, high concentration of carbon dioxide in the sea can give rise to the likelihood of upsetting the equilibrium of the aquatic life (Doney et al., 2009). To international and national concern, the one of the sources for which drives the concentration in seawater ominously uphill, besides mass onshore carbon dioxide release into the atmosphere, is the offshore natural gas extraction for which the issue of leakage arises. However, it is pertinent to point out that the major contributor of carbon dioxide emission originates from onshore anthropogenic activities dating back to pre-industrial revolution (Lüthi et al., 2008). Hence, it is best to study the effect of high carbon dioxide concentration on the aquatic due to greenhouse gas emission in order to paint a better picture of the prolonged effect of high carbon dioxide level in seawater.

It has been calculated that carbon dioxide level in seawater has witnessed a sharp increment as compared to those days when industrial based activities was still in its infancy. In the present, the carbon dioxide concentration in seawater is recorded within the range of 172e300 ppmv (Lüthi et al., 2008) in which the pH value underwent a decrease of 0.1 unit in consequence of the 30% upsurge in the hydrogen ions (Caldeira and Wickett, 2003; Raven et al., 2005). In a simulated study conducted by Caldeira and Wickett (2003), unconstrained carbon dioxide release is projected to exceed 1900 ppm by the year 2300 with the maximum pH value reduction up to 0.77 units. In addition, an analysis of air trapped ice cores indicates that the global carbon dioxide level in seawater from 420,000 years back to pre-industrial era, fluctuated between 180 ppmv and 300 ppmv until later in industrial revolution age, the level spiked up to 380 ppmv (Petit et al. 1999). This is certain to pose a disturbing impact of the aquatic life and fisheries which in turn, can jeopardize the source of livelihood of the local fishermen.

Based on a study conducted by Fivelstadet. al (2003), elevated level of carbon dioxide has been discovered to be damaging towards a particular type of salmon, Salmosalar L. which is to be found in abundance in northern Atlantic Ocean (Shearer, 1992). Apparently, "high levels of carbon dioxide in the water will reduce pH and increase the toxicity of aluminum causing hypertrophy and hyperplasia of the gill epithelium." Consequently, it reduces the feed conversion ratio and growth as well. Due to this finding, another study implemented by Martens et al (2006) to observe the effect on high carbon dioxide water on the same species of fish. The result implies that, under the range of 10mg/L to 35 mg/L of carbon dioxide concentration, the fish weight was recorded to be 20.9% lower than that of under normal condition.

Another investigative venture carried out by Bressanet. al (2014) manage to prove that "… ocean acidification may negatively affect the ability of marine organisms to produce calcareous structures while also influencing their physiological responses and growth". The central proposition of the study is that the production of marine calcifiers is retarded from producing calcareous skeletal structure as the result from changing carbonate chemistry (Fabry et al. 2008). This is a direct consequence of the upsurge concentration of carbon dioxide in atmosphere which is significantly higher than in normal condition throughout the rest of the history. An experiment was devised to put the hypotheses to the test, in which one of the two species of mussels were chosen because of the lucrative income resource for Italian aquaculture industry (FAO, 2012) and they are widely bred in Northern Adriatic regions. Henceforth, it was found that two out of the three proposed hypotheses, reduced survival and occurrence of shell injuries were positively confirmed from the obtained result.

Reef building corals and coralline algae are also predicted to undergo significant growth setback in response to the changing condition of seawater, especially the sudden increase of carbon dioxide level. Evidently, carbon dioxide, being an acidic component of the seawater is very much likely to alter the carbonate equilibrium of seawater, leading to reduced pH value and carbonate ion concentration (Kleypass and Langdon). Prior to testing, two postulations were made by Klaypess and Langdon, those are "an increase in total carbon dioxide in seawater results in a reduction in carbonate ion concentration" and "many independent experiments show a strong positive relationship between carbonate ion concentration and calcification rate in numerous species of calcifying algae, scleractinian corals, and coccolithophores.". The findings of the study show that reduction in calcification rates is highly probable in light of the changing chemistry of the seawater. Even though the biochemical mechanism for calcification is yet to be comprehended with assured confidence, it was safe to conclude that "dissolution of high magnesium calcite can potentially buffer the carbonate system in coral reef environments, particularly once seawater becomes undersaturated with respect to that mineral" in which it can potentially be the driving force towards the extinction of coral reefs.

With that, it is substantially established that, high content of carbon dioxide in seawater is certain to be of threat to the flourishing inhabitants of the ocean. Therefore, this paper is dedicated for modelling consequence study of carbon dioxide dispersion in seawater which in fact, is the central thesis of the paper. Deep-water carbon dioxide dispersion can be as the result of natural marine causes or anthropogenic activities (Dissanayake et. al, 2012) such carbon sequestration and natural gas pipeline leakage. As for natural underwater storage of carbon dioxide, the accidental releases can be in direct effect of opening fault on the crust such as carbon dioxide release in Lake Nyos, Cameroon which has raised the concern among environmentalist to study the impact of drastic increase carbon dioxide concentration and the ways and means to curtail such phenomenon in the future (Dissanayake et. al, 2012).

The mechanism by which carbon dioxide leaks from any man made carbon dioxide storage system is either via point-source or localised releases, or through a fault or fracture system present in the carbon dioxide bearing geological stratum (Jensen. N. B. et al, 2013). Due to the relatively low density of carbon dioxide in comparison with seawater; carbon dioxide that leaks from any opening will upsurge in the form of plume (QICS, 2012). Nevertheless, carbon dioxide is likely to dissolve in the seawater to dissociate into hydrogen and bicarbonate ions, before the plume can emerge on the surface. It, henceforth follows that myriad of marine life forms that rely on the bicarbonate or carbonate ions or impacted by pH, is susceptible to drastic change of the seawater chemistry (Blackford, 2013). As the result, the carbon dioxide rich region of the seawater has the tendency to sink as it has slightly higher density than normal seawater. Dispersion and dissipation of the plume will be carried away and throughout the ocean by the tidal mixing and natural current of the sea, while the sea floor depression and thermal stratification can act against the dispersion to slow it down. Myriad studies have been made available to public for which attest to such description of carbon dioxide dispersion behavior.

2.2 ASSESSMENT OF PRESENT CFD TECHNIQUES IN MODELING CARBON DIOXIDE TOXICITY RELEASE IN SEAWATER

Due to the scarcity of researches conducted on modeling the carbon dioxide dispersion from underwater pipeline leakage, the scope of the review is extended to accommodate studies of carbon dioxide dispersion from artificial or natural underwater carbon storage leakage. As matter of fact, numerous studies have been conducted pertaining to that problem as there has been rising concern over the fate of the life marine as well as the dangers of greenhouse gas emission into the atmosphere as the result of such phenomenon. Nevertheless, the pressing point that has the most bearing to the central thesis, such as single point source or dispersion model will be adequately emphasized throughout the review.

Leiferet. al (2006) has conducted a study on behavior of natural marine gas, methane seepage blowout in contributing towards atmospheric methane. An observation is made on Shane Seep as a result of volcanic activity, solely for the purpose of measuring the bubble plume's upward rush along water column by introducing a test dye to the opening of the leakage. It was discovered that as "bubbles plumes lift deeper, cooler, water that forms a divergent outward flow of water at the sea surface". The bubbles expand up to several meters in diameter as they reached 5 meters above the seafloor. Eventually, after several minutes, the flux dissipated slowly to approximately normal emissions. It was suspected, from this observation that, "chain burial likely occurred from multiple gas blowout". Based on the data obtained from this observation, numerical modeling is constructed for simulating the behavior of methane gas dispersion underwater in predicting the subsequent atmospheric condition.

The result of the numerical study underlines the importance of the rate of methane discharge as the determining factor whether the gas plume will escape into the atmosphere or not. The study also made it possible to show that, due to flowing wind of the atmosphere, the source of emissions can be detected by air pollution measurement station given huge enough bubbles were produced from the fault line. This should be deemed alarming as it can potentially give rise to drastic climate change due to massive release of methane into the atmosphere.

The study conducted by Dissanayake et. al (2012) revolves on the idea to construct a model (OCEAN_CO_2) for simulating carbon dioxide release from moderate ocean depth, either for single point or releases spread over an area (non-point source). The physiochemical processes accounted for in the dispersion model are the expansion of gas bubbles during the upward travel due to pressure changes, gas dissolution and its impact on bubble volume and density changes, and tracking the transport dispersion of dissolved and gaseous carbon dioxide. This model is utilised to simulate the natural carbon dioxide release as observed in Kagoshima Bay, Japan. OCEAN_CO_2 is the modified version of MEGADEEP model (Chen et. al, 2009) for which it was used to calculate the behaviour of methane and natural gases from single point of release. Using MEGADEEP its basis, adjustments were made upon it to be applied for dissolved carbon dioxide simulation and the resulting pH value.

The simulation period of the model was executed within two 168 hours (7-days) during fall and winter season at the selected location. The release rate is approximated to be 438 000 tonnes/year from an area of 0.8 km^2, which is in accordance to the most recent approximation by Harata et al (2010). The initial diameter of the bubbles used is 15 mm and its bubble size is categorized in spherical cap type as indicated by the formulation of the model. The plan view and the release area spanned over 900m x 900m with each grid cell of 900m x 900m x 10m in x, y and z direction respectively. This is in agreement with the observation made by Horibel et al. (1980). The velocity profile was taken from the data provided by Japan NUS Co., Ltd which was based on their hydrodynamic model and coincidentally bears similarity with COSMOS (Nakata et al. 1983 and Taguchi 1989). With regards to the input for temperature, salinity, and alkalinity profile, the data are taken from the measurement from Kagoshima Bay in times of winter and fall.

The result implied that, due to dissolution rate and transport being mainly dependent on bubble size, “the highest level affected does not change with moderate increases in discharges unless the increase is several orders of magnitude creating a jet condition”. Therefore, pH values are certain to drop at any given discharge rates and the density of carbon dioxide enriched seawater can be considered as negligible. The bottom line is the result from the simulation indicates excellent compliance with actual scenario observed in Kagoshima Bay. This is evident from the bubble dissolution and bubble velocity which compare reasonably well to the laboratory data. Even the pH calculation was verified with the measure field data. In a nutshell, the simulation of OCEAN_CO_2 model shows convincing match with the measure field data, which renders it reliable for simulating the given scenarios. Nevertheless, the drawback of this study is that it only accounts for carbon dioxide release of days to weeks, thus unsuitable for longer period of simulation. This owes to the fact that the computational times escalates rather exponentially as the simulation time is conducted longer than one week. Apart from that, improvements on data required so that it observes TCO_2 concentration and pH profiles because the boundary interaction of dissolved carbon dioxide is to be improved with more comprehensive investigation for real life field application.

In addition, Kano et al. (2009) has implemented a research on developing a numerical simulation for the prediction of CO_2 concentration change in the sea as the result of leakage from the underground aquifer, artificial carbon storage. Even though, it is not a study pertaining to single point release, it is does bear relevance to the central thesis in sense that the modelling process of carbon dioxide dispersion can be emulated and thus, is worth taken into consideration. The model was developed to simulate underwater carbon dioxide dispersion of two leakage rates, of which the extreme one is 94, 600 t/y under the assumption that a large fault line accidentally connected the carbon dioxide reservoir and the seafloor, and the moderate one is 3800 t/y, estimated from the seepage rate of an existing EOR site. It takes into account the behaviour of carbon dioxide bubbles, the dissolution, and advection-different fusion of dissolved carbon dioxide in its numerical simulation. A multi scale ocean model was developed from this study with the MEC ocean model (JASNOE, 2003) as its base model. This is owing to the additional feature of the model is that it takes into account of both hydrostatic and full-3D models for tides and current simulation on two different spatial scales i.e. 0(1-100 km) and 0(1-100m), respectively. Henceforth, an Eulerian-Lagrangian two-phase model was adopted and incorporated to the original MEC full-3d model so as to analyse the motion of the dispersed phase by way of solving the motion equation of individual bubbles.

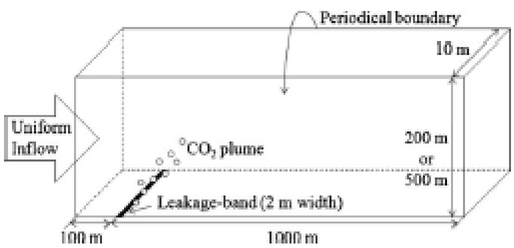

Figure 1: Schematic view of computational domain (Kano et al, 2009)

The simulated region for the computational conditions is the geological storage of carbon dioxide around Japanese coast (Lia et al, 2005) as it is known to have a fault line in the seafloor and a huge thermal power generator located at the seashore. The domain size of the hydrostatic model was 132km x 50 km with 33 x 25 x 48 grid while the full-3d model size was 4000 m x 2000 m x 118 m and the grids were 160 x 80 in in the x and y direction respectively, which was also adopted for the hydrostatic domain for the vertical column. The climate conditions were used according to the annual average recorded by the local observatory of the JMA in the year 2000 in order to calculate the sea-surface fluxes T and S. The "extreme" leakage rate, 94 000 t/y was chosen based on the migration of carbon dioxide calculated by RITE (2004) under the seabed when a fault created, by chance, between the seabed and carbon dioxide storing aquifer. Contrariwise, the moderate case of leakage rate, 38 000 t/y was adopted from the seepage rate recorded by EOR field in Rangley, USA. The initial diameter of the bubble was taken to be 2 cm as established by case studies performed by Kano et. al (2009).

The outcome of the simulation maintained that carbon dioxide bubbles after 10 days dissolved within 120 m of the vertical distance for both cases. Even so, the non-zero ΔpCO_2 is detected at the surface which could be in consequence of the strong upsurge of the carbon dioxide bubble plume. Therefore, it was believed that, based on the model developed, the carbon dispersion release from seafloor fault line would not pose a significant threat on the marine life residing on the seabed.

Furthermore, another relevant analysis was carried out by Dewar et al. (2013) which aimed at developing a model of two-fluid, small scale numerical ocean, which as proposed by Chen et al. (2003, 2005) with the purpose of simulating plume dynamics and increment of water acidity as the result of highly probable carbon dioxide leakage from sub-seabed reservoirs erupting, or pipeline rupturing into the North sea. In this study myriad scenarios are being modelled with the physio-chemical effects, by considering the movement and dissolution of the leaked carbon dioxide in accounting for the immense unpredictability of the location of the leak. The properties being studied for the simulation include the correlation of the drag coefficient of bubbles/droplets free rising in seawater and a sub-model in predicting the initial bubble/droplet size forming on the sea-floor. In regards to the geological setting of the study, local to the North Sea and the west coast of Scotland which is similar with that of Statoil's Sleipner Project.

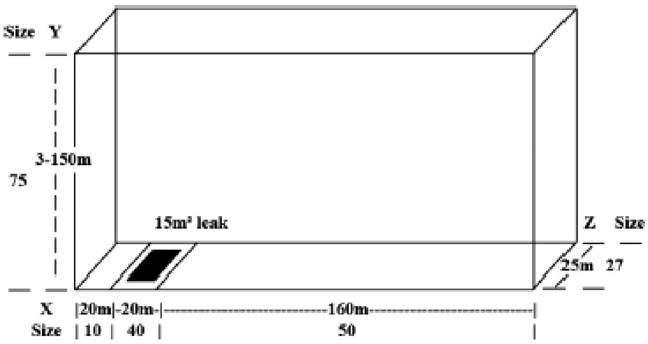

Figure 2: The computational domain (Dewar et al, 2013)

The domain area was set up in such as a way that “the mesh in the horizontal ‘x’ direction is 100 grid points in length with non-uniform grid distributions; this is concentrated around the leakage area where a mesh distance of 0.5 m is computed” whereas “in the vertical ‘y’ direction, a uniform grid is set with 75 equally spaced points where the total distance” so as to demonstrate “the full extent of the plume”. As for the ‘z’ direction, a uniform 25 grid points is used along with the leakage area of 15 grids. One to four case studies were employed to model the North Sea shelf mapped at 100 m while the next five to six case studies were employed to model Norwegian Channel and Skagerrak at depth of 320 m and 600 m. seven and eight case studies were reserved for comparing the conjecture of a shallow depth leakage with the experiment on the west coast of Scotland. The initial bubble or droplet plume was assumed to between 5.0 mm and 8.0 mm. For wave height and velocity at the open boundaries of hydrostatic model domain, the non-reflection boundary condition proposed by Hino and Nakaze (1989) was adopted. The tidal prediction model of Matsumoto et al. (2000) was utilised for the wave direction input.

For most of the case scenarios, the carbon dioxide upsurges from the leakage will dissolve in seawater before reaching to the surface (first two and half minutes for all cases except Skagerrak, which took up 30 minutes full before reaching terminal velocity). Carbon dioxide leakage in the shallow water was shown to have been a tremendous peril towards the marine life in the west coast of Scotland due to the lack of large current homogenizing the gas concentration throughout the seawater as well as the fast dissolution rate. Carbon dioxide release in the deep ocean such as Skagerrak case was recorded to have the largest bubble/droplet height as a percentage of leakage depth. This is because there is far less risk of release at the seawater surface and return back into the atmosphere, but it will give rise to the greater distribution within the ocean. Henceforward, it is safe to conclude that shallow, and low current carbon dioxide leakage poses a major danger upon aquatic organisms seeking sanctuary there. It was predicted, though not considered in the study, that large bubble produced from the shallow, low current leakage has the highest probability of escaping the sea into the atmosphere. The effects of this study is restricted a very small scale as compared to the total volume of the waters in the medium to long term in the regional scale. In fact, it is almost an impossibility to pinpoint where or scales of the possible leakage, thus indicating that the result is merely a prediction alone. Due to high cost and difficulty of field experiments, the experiment is restricted in terms of pressure, thus requiring models that capable of filling in the gap. Nevertheless, the field data from the QICS experiments and the coming small-scale in situ experiment should come in handy for providing a prediction of the experimental results, as well as the essential data for calibration of the model and validation of usefulness of the model.

Another investigative venture was carried out by Blackford et al. (2013) to study the environmental impact of seepage from carbon capture and storage reservoir and the proper design procedure for the monitoring tools is dependent on the understanding of the dispersal carbon dioxide plume in seawater. Fine scale model of marine hydrodynamics was adapted to be inclusive of relevant carbon dioxide processes by combining the approaches proposed by Blackford et al. (2008)and Chen et al (2005) with Blackford et al. (2009). Varying leak scenarios was taken into consideration for the simulation while testing the aftermath of tidal viability and model configuration. This study also purported that aquatic organisms with limited migration capability were likely to confront the worst jeopardy in consequence of the carbon dioxide dispersion since the carbon dioxide enriched seawater tends to be more localised and located at the bottom the water column.

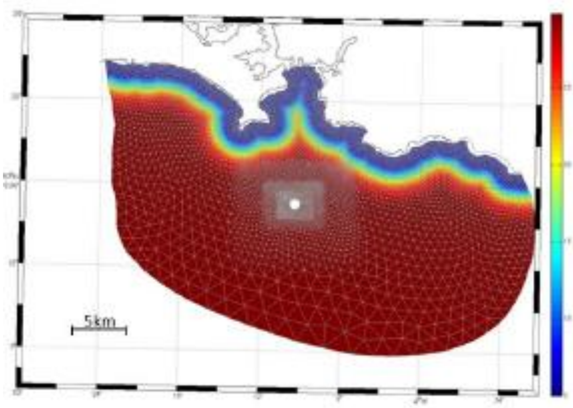

Figure 3: Bathymetry and grid design for the idealized domain. Depths are in meters. The leak point is marked in white (Blackford et al, 2013)

The modeling tools being used to simulate the behavior of carbon dioxide leak was Finite Volume Coastal Ocean Model (FVCOM) (Chen et al, 2011 and Torres et al, 2011), coupled with Carbonate system model to forecast chemical changes subjected by the influx of carbon dioxide. The North West European shelf was taken as the ideal domain for it makes up of “an irregular coastline inclusive of a large bay and coastal promontory”. The description of the domain was demonstrated as follows. The domain developed spanned over $674km^2$ of area in which the coastline has a nominal resolution of 150m while the ocean boundary has a 1 km resolution. The leakage being tested had a side length of 500m, and resolution was fine-tuned by setting up a second mesh which sloped down to $2541m^2$ or $0.0025km^2$ with a side length of 70m. For the sake of simplicity, the temperature and salinity were fixed at 13^oC and 35 salinity units which were consistent with North West European Shelf. Other external forces such as wind, river or surface heating were neglected from the simulation. The simulation period was around one month to cover two spring cycles. The depth of leakage was taken at nominal 30 m which were located about 15 km away from the coastline. The scenarios of the simulation included dissolved point with low source, dissolved point with source high and pipeline rupture. The mean current velocities are taken at 0.10m/s, 0.14m/s, and 0.17m/s to be tested these three scenarios.

The result, which was presented as time evolution maps of leakage, showed that monitoring of carbon dioxide dispersion leakage is rather a cumbersome task given the fact that tidal mixing in North West European shelf is very strong. However, the general pattern is that bubble plume dissipated before reaching the sea surface as the result of dissolution. It was also discovered that any leak occurrence was likely to differ from one another when other factors such as the state of tide, wind driven mixing, geographical location, leak amount and duration of leak are taken into consideration, which makes it rather difficult to produce a reliable prediction of outcome. Nonetheless, the study provided here is only a humble attempt at modelling the carbon dioxide dispersion using limited data available for carbon capture in Malaysia region as the project is still in development stage, and thus requiring further tweaking as it was not designed to account for all possible scenarios.

2.3 SUMMARY

Table 1: Summary of Parameters and setting used in published literatures

Author	Scenario	Simulation setting	Medium Condition	Bubble and leakage characterization	Findings
Leifer et. al (2006)	Seepage on volcano active area (Shane seep)				Rate of release as factor for gas escaping sea surface
Dissanayake et al (2012)	Kagoshima Bay, Japan	Duration: 168 hours during fall and winter	Area: 0.8 km2	Initial diameter: 15 mm Bubble size: Spherical cap type Release rate: 438,000 t/y	Bubble size is the main factor. The pH will drop at any given rate Density change of water is negligible. Consistent with data from Kagoshima Bay (pH depression localized within 120 m)
Kano et. al (2009)	Japanese coast geological storage	Duration: 10 days	Domain size: 132 km × 50 km with 33 × 25 × 48 grid, 4000m × 2000m x 118m	Initial diameter: 2 cm Release rate: 38000 t/y to 94600 t/y	Dissolve within 120 m vertical distance. Non-zero concentration of CO_2 detected at the surface Threatens floating marine life, and nearby leak

Dewar et al (2013)	Sub seabed reservoir in North Sea	Place: 1 - 4 case: North Sea Shelf 5 – 6 case: Norwegian Channel (320 m) and Skagerrak (600m) 7 – 8 case: West Scotland coast	Wave height and velocity: Hino and Nakaze (1989) Wave direction: Matsumoto et al (2000)	Initial diameter: 5 mm and 8 mm	Dissolve within 31% total depth of sea Larger bubble produced has the highest probability of leaving sea surface. Low current leakage are the most dangerous to marine life
Blackford et al (2013)	The North West European Shelf	No other external force present Duration: 1 month, covering 2 springs cycle Location: 15 km offshore	Domain area: $674km^2$ Temperature: 13^oC Salinity: 35 units 3 tidally driven mixing regimes with mean velocities: 0.10m/s 0.14m/s 0.17m/s	Leakage area: Side length of 500 m Depth: 30m Leakage type: Point with high source Point with low source Pipeline rupture	Bubble plume dissolve before reaching the surface Leakage behavior differs in terms of state of tide, wind driven mixing, geographical location, leak amount and duration of leak Leaks tend to be localized, threatens immobile marine life living nearby the leak

CHAPTER 3

METHODOLOGY

3.1 DEVELOPMENT OF FLUID DOMAIN

The fluid domain is developed based on the research conducted by Dewar et al (2013) which aims at modeling the small scale physiochemical impacts of carbon dioxide leaked from sub-seabed reservoirs or pipelines within the North Sea and surrounding waters. This is owing to the fact that the study is aiming towards simulating the effects that are confined to a very small scale in comparison to the total volume of the waters, making it practical to be implemented within the scope of the final year project. Such a domain is selected because each of the numerical calculations can be worked through use of discrete counterparts of the model at each grid location within the domain of the three dimensional mesh systems. The mesh sizing of the fluid domain is set up as follow:

i. 100 uniform grids in horizontal x direction representing length of 200m, and mesh distance of 0.5m is concentrated around the leakage area of $15m^2$.
ii. 75 uniform grid in y direction representing a depth of 150m
iii. 25 uniform grids in z direction representing a width of 25m

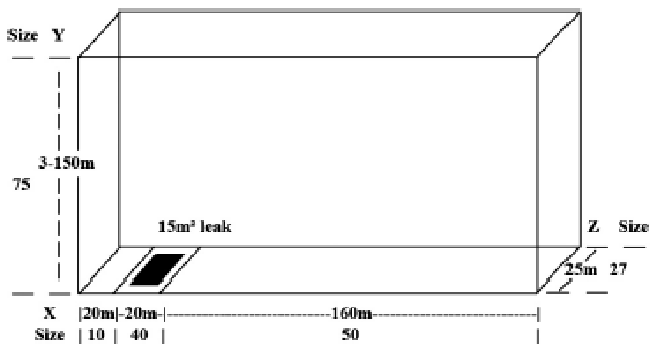

Figure 4: Selected computational fluid domain for ANSYS Fluent simulation

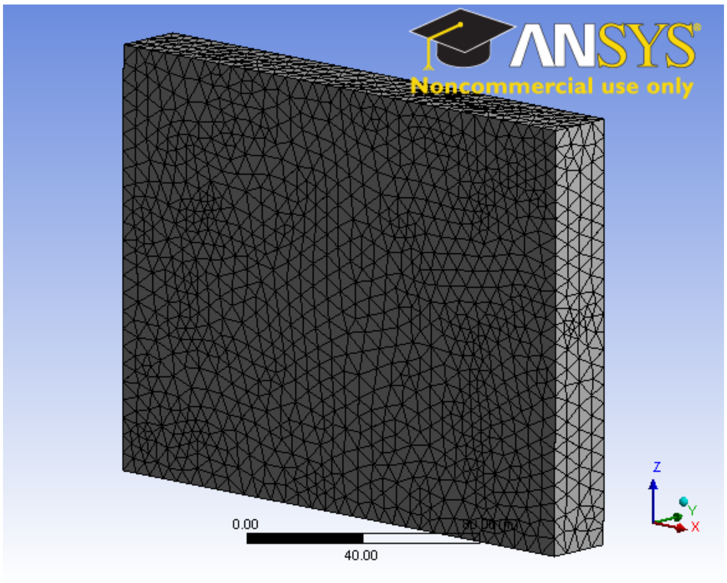

Figure 5: The resulting fluid domain developed in ANSYS Fluent.

For boundary conditions setting, which is available in name selection option, the right and left sides are set to inlet and outlet respectively. This implies that that movement of seawater current will in x-direction only. The bottom boundary is set to wall condition to represent solid ground. The leakage area is also set to inlet to enable movement of CO_2 plume. Finally, the front, back and top sides are set to symmetry. The number of elements achieved is 26,892 units

3.2 DEVELOPMENT OF COMPUTATIONAL FLUID DYNAMICS

3.2.1 Governing equation for seawater

Dewar et al (2013) makes use of the small turbulent ocean, modeled and reconstructed by means of large Eddy Simulation (LES) which is the continuity equation, with mass exchange rate.

$$\frac{\partial \bar{\rho}}{\partial t} + \frac{\partial \bar{\rho} u_i}{\partial x_i} = w_c \tag{1}$$

The LES Navier-Stokes equation with exchange rate of momentum and the sum of external forces from LES dissipation rate and buoyancy is incorporated into the above equation to compute the initial vertical density distribution and hydrostatic pressure through $\mathrm{p} = \mathrm{P} - \mathrm{p_h}$ and $\partial \mathrm{p_h} / \partial \mathrm{x_i} = \rho_o \mathrm{g_i}$.

$$\frac{\partial \bar{\rho}_d u_{dj}}{\partial t} + \frac{\partial \bar{\rho}_d u_{di} u_{dj}}{\delta x_j} = \alpha_d (\bar{\rho}_d - \rho_w) g - \dot{F} \tag{2}$$

The changes in scalar quantities, including temperatures, salinity and CO_2 concentration of the carrier fluid are expressed by scalar transportation equation, provided by the scalar gradient, LES turbulent diffusivity, and mass exchange term (for CO_2 concentration):

$$\frac{\partial \bar{\rho}\varphi_k}{\partial t} + \frac{\partial \breve{\rho}\varphi_k u_j}{\partial x_i} = \frac{\partial}{\partial x_j}\left(\bar{\rho} D_k \frac{\partial \varphi_k}{\partial x_j}\right) + \frac{\partial \bar{\rho} q_k}{\partial x_j} + w_c \tag{3}$$

3.2.2 Governing equations for leaked CO_2

The equation is developed with the assumption that the bubbles or droplets acts as quasi-continuous fluid based on a two-phase Eulerian-eulerian model, the dynamics of the CO_2 can be assumed to flow as a continuous fluid plume. Also, the interactions through fluid particles merging or breakup are ignored and convection model is utilized to model the change of CO_2 volume with time as the bubble rises to the surface. The CO_2 momentum balance used to calculate the bubble or plume velocity is similar to that of seawater phase owing to the buoyancy force between CO_2 bubbles or droplets and seawater and drag force, as in **equation (2).**

3.2.3 Reaction

As the dissolution of CO_2 bubble plume into the seawater is predicted to take place, a chemical reaction by which CO_2 and water mix to produce carbonic acid, and dissociates into bicarbonate ions HCO_3^-, carbonate ions CO_3^{2-}, hydroxide ions OH^- and hydrogen ions, H_+ by the International Union of Pure and Applied Chemistry (IUPAC).

$$CO_2 + H_2O \Leftrightarrow H_2CO_3$$

$$H_2CO_3 \Leftrightarrow H^+ + HCO_3^- \Leftrightarrow CO_3^{2-} + 2H^+ \tag{4}$$

Owing to this, it follow that the moles of hydrogen ions produced is dependent upon the moles of carbon dioxide dissolved, along with their dissociation constants, based on pressure and temperature:

$$\sum CO_2 = \left(\frac{[H^+]}{[H^+]+2K_2}\right).\left(1 + \frac{K_2}{[H^+]}.\frac{[H^+]}{K_1}\right).\left([H^+] - \frac{K_w}{[H^+]}\right) \tag{5}$$

With $\sum CO_2$ as the total carbon dioxide concentration (mol/l), $K_{i=1,2}$ are the constants for the dissociation of carbonic acid and K_w is the ion content of the water. The generation of positive hydrogen ion decreases the pH, implying the acidity of the seawater increases accordingly, which is calculated through the logarithm of the ion content:

$$pH = -log_{10}(H^+) \quad (6)$$

3.2.4 ANSYS Fluent Mathematical Model

Based on this correlation, the model used for the simulation is mixture, large eddy simulation (LES) for multiphase and viscosity model respectively, because they are at best more consistent with the setting used in Dewar et al (2013). Large eddy simulation based governing equation is utilized to model seawater carrier phase and dispersed bubble phase. In fact, Dewar et al also makes use of this technique to model the turbulent transportation of and CO_2 which entails the dissipation, diffusivities. Large eddy simulation is the most reliable technique for simulating turbulence for incompressible flows as it enables the large eddies of the flow to be dependent on the geometry.

This particular vicious model is only available with mixture multiphase model with two Eulerian phases to represent seawater and carbon dioxide, which is compatible with the intended setting. It can be utilized to model multiphase flows where the phases move at differing speeds, yet local equilibrium over short spatial length scales. This is important because the carbon dioxide bubble plume is expected to homogenize with the primary phase (seawater) over a certain vertical distance and thus reaches a steady state. The mixture model can model phases (fluid or particulate) by solving the momentum, continuity, and energy equations for the mixture, the volume fraction equations for the secondary phases, and algebraic expressions for the relative velocities.

As for the reaction, species transport is incorporated with volumetric reaction type is selected for simulating the reaction between CO_2 and seawater. Finite-rate/eddy dissipation is selected to simulate the turbulence presence during the mixing of the two species whereby Arrhenius, Eddy-dissipation, and reaction rate are computed.

Arrhenius equation

$$k_{f,r} = A_\gamma T^{\beta_\gamma} e^{-\frac{E_\gamma}{RT}} \quad (7)$$

Where,
A_γ = pre-exponential factor
β_γ = Temperature exponent
E_γ = activation energy for reaction
R = Universal gas constant

Eddy dissipation model

$$R_{i,r} = v_{i,r}^{t} M_{w,i} A\rho \frac{\varepsilon}{k} \min \mathcal{R} \left(\frac{Y_{\mathcal{R}}}{v_{\mathcal{R},\gamma}^{t} M_{w,\mathcal{R}}} \right) \quad (8)$$

$$R_{i,r} = v_{i,r}^{t} M_{w,i} AB\rho \frac{\varepsilon}{k} \left(\frac{\sum PY_{P}}{\sum_{j}^{N} v_{j,r}^{tt} M_{w,j}} \right) \quad (9)$$

Where,
Y_P = the mass fraction of any product species, P
$Y_{\mathcal{R}}$ = the mass fraction of a particular reactant, $\mathcal{R}$
A = an empirical constant equal to 4.0
B = an empirical constant equal to 0.5

Reaction rate equation

$$k_{net} = k_{low} \left(\frac{1}{1+ p_{\gamma}} \right) F \quad (10)$$

Relevant inputs are included in the reaction definition such as reaction rate exponent, and stoichiometry coefficient, pre-exponential factor and activation energy for the chemical equation (4). These values are also acquired from the IUPAC.

3.2.5 ANSYS Fluent Simulation Setting

The following is the data pertaining to the properties of seawater and CO_2 to be input for the simulation.

Table 2: Summary of parameters and setting used for CO_2 toxicity modeling in ANSYS Fluent

Properties	Seawater	Carbon Dioxide
Density (kg/m^3)	1027.72 (ITTC, 2011)	1.7878
Viscosity (Pa.s)	0.001620 (ITTC, 2011)	-
Initial bubble size (m)	-	0.008 (Dewar et al, 2013)
Velocity	Average current velocity: Southwest monsoon - 0.4 m/s (Fadzil, 2012)	Release rate : Upward - 1.18 m/s (Dissanayake, 2012)
Temperature	5℃ (Chern & Wang, 1998)	-

The modeling is made to apply the condition of South China Sea using certain other setting adopted from other studies. The current velocity of the seawater is taken to be at 0.4 m/s during Southwest monsoon (Fadzil, 2010). The temperature is taken to be at 5℃ which is in accordance with graph of depth versus temperature as produced by Chern & Wang (1998) at a depth of 1212m, which is the average depth of South China Sea. The release rate of the CO_2 is taken to be 1.18 m/s, to emulate the worst case scenario of sub-seabed leakage (Dissanayake, 2012).The initial bubble size is taken as 8mm, to emulate the study conducted by Dewar et al. The model is used to simulate the condition of carbon dioxide leakage after 1 hour.

3.3 VERIFICATION AND VALIDATION

The compatible case study from Dewar et al selected for comparison with ANSYS Fluent simulation result is the Skagerrak localized waters. In **Table 3,** it can be seen that the height of the dispersed plume rise is about half of the depth of the fluid domain and the maximum difference of pH value is recorded nearby the leakage area as per **Figure 8**.

Table 3: The results of leaked bubble/droplets dispersed rising height and maximum pH and CO_2 concentration.

	Dispersed plume rise height (m)	Maximum ΔpH	Maximum CO_2 concentration (ppm)
The Skagerrak	71.23	-1.09	9.27E+9

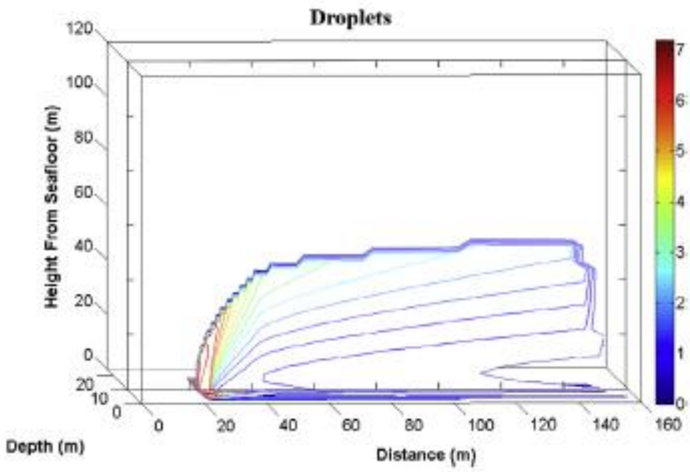

Figure 6: The Skagerrak – summer at 600 m depth (droplets) against bubble diameter

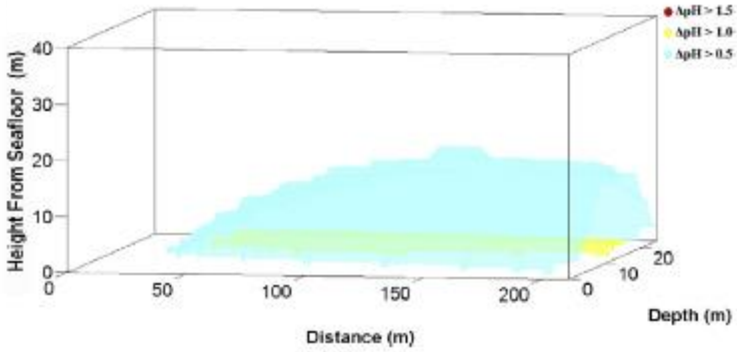

Figure 7: Three dimensional of reduction in pH caused by the dispersed CO_2 after 1 hour leak

Source: Dewar et al (2013)

It is imperative to emphasize once again that currently there are no directly related studies made previously pertaining to this topic. Owing to that, any graphical result obtained from previous case studied should not be relied on in totality for it does not operate in the same parameters and scenarios used for this project. However, these previous case studies also help in providing the overall observation to be expected from the simulation of carbon toxicity release in ANSYS Fluent.

Since it is impossible to predict the location and the scales of the leaks, thus the simulation result acquired is merely a projection on its own to fill in the gaps in the result of the experiments. However, it is pertinent to emphasized again that the correlation developed in Dewar et al (2013) is based on the observation from the experiments for estimation is made predict the best modeling of CO_2 fluid dynamics. As for this, the simulation result by Dewar et al alone can be made as the reference for validation of the ANSYS Fluent simulation result. Overall, the simulation result by Dewar et al (2013) suggests the CO_2 bubble plume dissolved within 31% of the total depth of the sea. Even so, it is predicted that large bubble produced from the leakage has the highest probability to leave the sea surface and emerge into the atmosphere albeit very rare. Consequently, low current leakage is the most dangerous to marine life, as the mixture of CO_2 with seawater produces an acid carpet covering the seafloor due to higher density. This acid carpet will take time to dispersed through the sea as it tend to localized with certain area and depth of region which in turns pose a significant danger towards marine life.

Owing to the fact that ANSYS Fluent does not provide the result in terms of pH value and bubble diameter, certain formula modification is required to make the two results comparable. Bubble diameter is related to volume through the formula of spherical volume.

$$V = \frac{4}{3}\pi(\frac{d}{2})^2 \tag{11}$$

From this formula, the relationship between volume and bubble diameter can be derived, whereby the two parameters are directly proportional to the other.

$$V \propto d \tag{12}$$

Therefore it should follow that increment of bubble diameter results in the increment of volume fraction. As for pH value given in Dewar et al (2013), it can be converted into concentration of CO_2 via **equation (5)** and **(6)** in terms of mol/L. With that, volume fraction from ANSYS Fluent and pH value of Dewar et al (2013) are to be computed using Microsoft Excel and converted into parts per million (ppm) for ease of comparison.

CHAPTER 4

RESULTS AND DISCUSSION

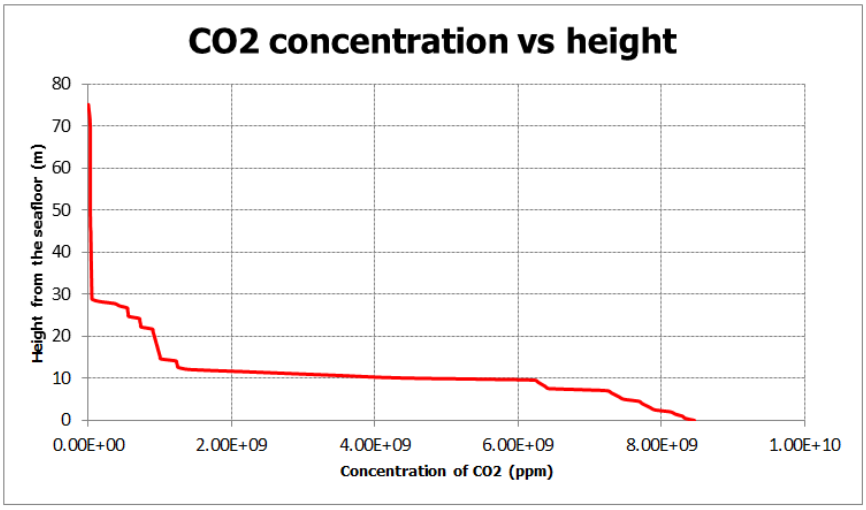

Figure 8: Graph of CO_2 concentration against height

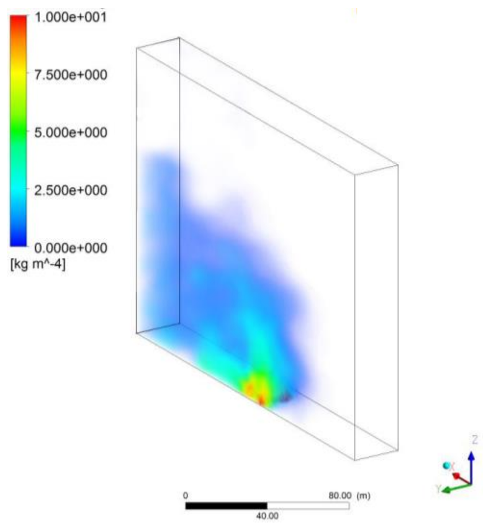

Figure 9: ANSYS Fluent volume rendering of density gradient of CO_2 in seawater

Based on the acquired ANSYS Fluent model of CO_2 toxicity release in seawater, it can be deduced that as the density of the solution increases as the depth progresses towards the leakage which result in the bubble plume falling back to the seafloor and localized within a certain depth instead of moving all the way upward to the surface as per **Figure 9**. This is in agreement with the findings of Dewar et al (2013) whereby the acid carpet is formed due to the difference the density between the acidic solution and that of the surrounding seawater condition. The maximum concentration of carbon dioxide from ANSYS Fluent is about 8.5E+09 ppm, which yields an error percentage of 8.2%. This indicates that the ANSYS simulation result is in conformance with Dewar et al (2013) model, which goes on to show that precious marine life inhabiting on or nearby the seafloor is exposed to the danger of high CO_2 concentration.

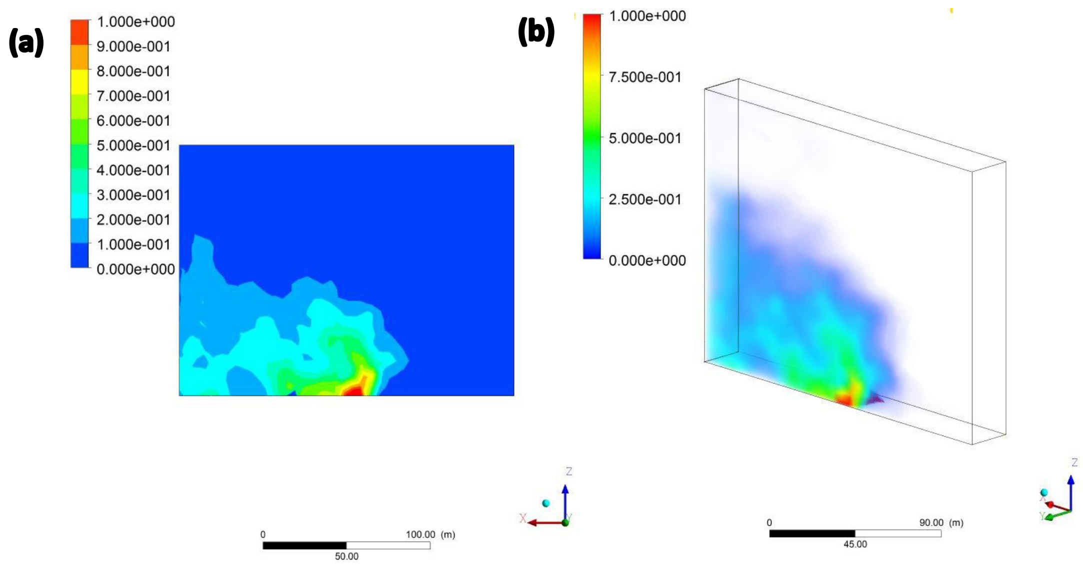

Figure 10: (a) ANSYS Fluent contour of CO_2 volume fraction from leakage area (b) ANSYS Fluent volume rendering of CO_2 volume fraction from leakage area

Furthermore, the bubble distribution form the ANSYS Fluent simulation is somewhat similar with the CO_2 release modeling by Dewar et al (2013) which indicates the size of bubble diameter decreases with height from the seafloor. In terms of volume fraction as per the simulation result from ANSYS Fluent, the value clearly display consistent also decrement with height, meaning that the CO_2 bubble plume will not emerge from the surface of the seawater and will dispersed throughout the ocean by the current velocity. The minor difference to be pointed out is that the highest disperse plume rise in Dewar et al is put at 71.23 m while that of the ANSYS Fluent is approximately 75.12 m, which yields a percentage error of 5.5% which is within acceptable range.

However, the pressing issue to be highlighted is that the contour pattern is significantly different from that CO_2 toxicity modeling of Dewar et al (2013). In addition, it can be seen that the bubble diameter over a distance of 120m after the point of leakage, is large at the top than that of the bottom, indicating that the volume fraction is larger in the upper layer of the plume than that of the lower as per **Figure 6**. On contrary, ANSYS Fluent simulation result yield a different contour pattern whereby the, on average, the volume fraction in the lower part is higher than of the upper part of the CO_2 bubble plume as per **Figure 10**. This is mainly due to the significant difference between the mathematical models available in ANSYS Fluent than the one user-defined by Dewar et al (2013). As mentioned earlier, the mathematical model adopted in Dewar et al (2013) is tailored in such a way to fill in the gaps of the details that is not discernible from the experiment. However, the model used in ANSYS Fluent is the selected as closely as possible with the Dewar et al (2013), therefore significant difference in the flow pattern should be expected. Apart from that, certain values of parameter applied in the ANSYS Fluent pattern is different from the one in Dewar et al (2013). For instance, the condition of the seawater in South China Sea is different from that of the North Sea Shelf condition in terms of temperature. Besides, the average current velocity used in Dewar et al (2013) is 0.01m/s whereas for ANSYS Fluent simulation, which is made to be in accordance with South China Sea condition, is 0.4 m/s. In addition, the leakage rate used in Dewar et al for Skagerrak case study is 0.0405 kg/s while for ANSYS Fluent simulation, in order to emulate the worst case scenario condition, leakage rate of 1.18 m/s is used. Therefore, it should be justified as to why the contour pattern is slightly different from the prediction in Dewar et al (2013).

CHAPTER 5

CONCLUSION AND RECOMMENDATION

In conclusion, this project is imperative as it aims towards developing the most reliable simulation model for carbon toxicity release in seawater along with the correct setting and data input. The simulation result from the model available in ANSYS Fluent is consistent with the previous studies in terms of certain aspects, such as the highest dispersed bubble plume, the formation of acid carpet on the seafloor and the maximum concentration of carbon dioxide. However, slight but notable under-prediction in terms of contour patent is to be expected due to the limited mathematical correlation available in ANSYS Fluent. This is owing to the fact, the mathematical correlation utilized Dewar et al (2013) are manually developed based on the parameter obtained from the experimental observation so that the model acquired is matched more accurately with the result of the experiment. This is certainly one of the features lacking in ANSYS Fluent due to the fact that existing model available may not be able to be utilized for specific parameters but the user defined function should be developed instead. However, such option is not taken into consideration as it is out of the scope of the project.

Apart from that, since there is not any reliable study conducted on pipeline leakage it is hoped that such as this research can be repeated to simulate the said condition when the experimental data is available for verification and validation. This is crucial so as to take into account all possible scenarios during CCS project execution so that proper measures and risk assessment can be put in place to contain the environmental hazard. User defined mathematical model should be developed in order to obtain the most accurate fluid contour pattern as per the experiment. Even so, it is also hope that this research can be of use for value-added data to those responsible in executing carbon capture storage system project.

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